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Effects on the fluid interface fluctuations due to the interaction potential form: Exponential interactions

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In this work, we investigate nonlocal effects (associated with exponential interactions) on the fluctuation properties of liquid films that completely wet random rough surfaces. It is found that the potential form and effective range could have significant impact on the real space fluctuation properties. The rms interface amplitude shows a complex dependence as a function of the potential effective range b which is characterized by a maximum at length scales smaller than the liquid film thickness. Comparisons with results obtained within the Derjaguin approximation shows that the nonlocal effects are more pronounced for slowly decaying interactions. [S0163-1829(98)00820-0]

Wetting of fluids on solid substrates has been an important topic of applied and fundamental research for more than a century. The complexity of the involved phenomena is rather cumbersome since wetting is sensitive to roughness and chemical contaminants of the solid substrates.[1–4] Significant insight into the influence of surface roughness has been gained by studies performed within the so-called Derjaguin (D) approximation.[2–5] The D approximation accounts for replacing the local disjoining pressure Π_d by that of a uniform film of thickness $h(r)$-$z(r)$ [with $z(r)$ and $h(r)$ being, respectively, the substrate and liquid-vapor surface profile functions] for small substrate roughness amplitudes, and then linearizing the disjoining pressure around the average film thickness ε on a flat surface.

Nonlocal effects lead to strong (exponential) damping of short-wavelength fluctuations and were taken into account in terms of a linear approach for random substrate roughness, while nonlinear contributions were investigated for periodically corrugated surfaces.[1] Generally, these effects are expected to have a small contribution for film thickness smaller than the healing length ζ (which characterize the competition of surface tension and disjoining pressure), and for $z(q)$ relatively large at $q\varepsilon<1$.[1,3] In this case, the Lorentzian damping (characteristic of the D approximation) substantially eliminates the small wavelength fluctuations and the liquid/vapor interface roughness is dominated by the fluctuations at $q\varepsilon<1$.[1,3] For a rough self-affine substrate morphology without a natural roughness cutoff (correlation length), the surface is rough at all length scales and the interface follows the substrate morphology at wave vectors $q\varepsilon<1$ and $q\zeta<1$ and the D approximation gives the effective cutoff correctly if $\varepsilon<\zeta$.[1]

The common case that is usually considered to study the influence of substrate roughness on interface undulations (by taking into account nonlocal effects[1,7]) is that of van der Waals interactions.[6] These interactions are of fundamental importance in wetting phenomena since they occur universally and fall off more slowly at large distances than other interactions.[1,6,8] In this case, nonlocal effects could yield a significant contribution on the real space fluctuations properties of the interface.[7] Nonetheless, the large healing length (thick films) asymptotic behavior of the interface amplitude still follows the power law $\sigma_w \sim \zeta^{-2}$ which was predicted within the D framework (ignoring nonlocal effects[9]).

The inverse power-law potentials used in previous studies do not possess an intrinsic length scale, and as a result the film thickness ε is the only length scale that controls the damping of long wavelengths ($q\varepsilon \gg 1$) due to nonlocal effects.[1] Although similar qualitative results are also expected for finite range potentials,[1] the actual influence of the nonlocal effects associated with finite range interactions on experimentally measurable real space interface fluctuation properties (e.g., with x-ray reflectivity)[10] requires a more detailed investigation. The latter is still missing and will be the subject of the present work. This will be accomplished by a simple direct calculation of the rms interface width and local interface slope assuming self-affine rough substrates. Finally, comparisons with the results obtained within the D approximation will be performed to determine the regime of film thicknesses where significant contributions occur due to nonlocal effects.

The substrate-liquid and liquid-vapor interfaces are considered random single valued functions of the in-plane position vector $r=(x,y)$ such that $\langle z(r)\rangle=0$ and $\langle h(r)\rangle=\varepsilon$. For weak interface fluctuations ($|\nabla h(r)| \ll 1$), and in the absence of thermal fluctuations, the interface height profile is given alternatively in real and Fourier space by[1,3]

$$\zeta^2 \nabla^2 h(r) = [h(r)-\varepsilon] - \int K(r-p) z(p) d^2 p;$$

$$h(q) = K(q)(1+q^2\zeta^2)^{-1} z(q) + \varepsilon\,\delta(q), \qquad (1)$$

with $\zeta=[\gamma/\int U(r,\varepsilon) d^2 r]^{1/2}$ the healing length which determines the length scale below which short-wavelength fluctuations are damped by the liquid-vapor surface tension γ. $U(r,z)$ is the interaction potential which is described by pair interactions between the molecules of all phases. Finally, the functional $K(r)$ in Eq. (1) is given by $K(r) = U(r,\varepsilon)/\int U(r,\varepsilon)d^2r$. In the D approximation $K(r)\sim\delta(r)$ which yields effectively $K(q)=1$.[2,3]

We will consider in the following finite range interactions of the form $U(R)=Ce^{-(R/b)^n}$ $(n=1,2)$ with b their intrinsic length scale (effective interaction range) and $R=(z^2+r^2)^{1/2}$.[1] Exponential interactions (especially the case $n=1$; simple exponential) have been discussed in the context of the wetting transitions, double-layer forces in water solutions against ionizable surfaces, etc. (for a review see Ref. 4). Moreover, following the authors of Ref. 1 we consider in the present study both Gaussian and simple-exponential interactions in order to study effects of short-range forces on interface fluctuations properties in a more general framework.

For Gaussian $(n=2)$ and simple-exponential $(n=1)$ interactions, we obtain in Fourier space for $K(q)$ (Ref. 1)

$$K_g(q)=e^{-(qb)^2/4}; \quad \zeta_g=(\gamma/C_g\pi b^2)^{1/2}e^{\varepsilon^2/(2b^2)}, \tag{2}$$

$$K_e(q)=\frac{\varepsilon(1+q^2b^2)^{1/2}+b}{(\varepsilon+b)(1+q^2b^2)^{3/2}}\,e^{-(\varepsilon/b)[(1+q^2b^2)^{1/2}-1]};$$

$$\zeta_e=(\gamma/2\pi C_e)^{1/2}[b(b+\varepsilon)]^{-1}e^{\varepsilon/2b}, \tag{3}$$

where there is not any dependence of $K_g(q)$ on the film thickness ε. Equations (2) and (3) indicate that steeper decaying potentials lead to a more rapid decay of $K(q)$ at large q, and healing lengths that increase more rapidly with film thickness. The latter implies that the crossover to the surface tension dominated regime occurs at smaller film thicknesses.[1]

The substrate roughness will be modeled as self-affine roughness which is observed in a wide variety of thin solid films.[11,12] The roughness fluctuations $z(r)$ are characterized by the rms amplitude $\sigma=\langle z(r)^2\rangle^{1/2}$, the correlation length ξ, and the roughness exponent H $(0<H<1)$ which is a measure of the degree of surface irregularity.[11,12] For self-affine surfaces, the roughness spectrum $\langle|z(q)|^2\rangle$ can be modeled for simplicity by the analytic form $\langle|z(q)|^2\rangle=[A/(2\pi)^5]\sigma^2\xi^2(1+aq^2\xi^2)^{-1-H}$ (Ref. 13) which interpolates between the self-affine asymptotic limits $\langle|z(q)|^2\rangle\propto q^{-2-2H}$ if $q\xi\gg1$, and $\langle|z(q)|^2\rangle\propto$const if $q\xi\ll1$.[11,12] A is the macroscopic average flat area, $Q_c=\pi/a_0$ with a_0 to the order of the atomic spacing, and the parameter a is given by $a=(1/2H)[1-(1+aQ_c^2\xi^2)^{-H}]$ if $H>0$, and $a=(\frac{1}{2})\ln(1+aQ_c^2\xi^2)$ if $H=0$ (logarithmic roughness).

Despite the fact that we will restrict our presentation to a specific substrate roughness exponent H (in the mean field regime $H<1/2$ (Refs. 1 and 2)), similar results will hold for other values of H (as far as the effect of the potential form and interaction range is concerned) since they will influence mainly the magnitude of the interface amplitude and local slope.[9] However, the consideration of self-affine roughness over finite length scales (ξ finite) is crucial for the correct determination of the liquid interface fluctuation properties under the influence of realistic substrate (random) roughness configurations.[12]

Initially, we will comment on the weak fluctuation regime since Eq. (1) applies for small local slopes $(|\nabla h|\ll1)$ or $\rho\equiv\langle|\nabla h|^2\rangle^{1/2}\ll1$.[1,14,15] In addition, in order the linear approximation to be hold, the local thickness of the film must be small $(|h(r)-z(r)|\ll\varepsilon)$ for power-law potentials, while exponential potentials introduce another relevant length scale.[1] Upon substituting the Fourier transform $h(r)=\int h(q)e^{-iq\cdot r}d^2q$ and considering translation invariance or $\langle h(q)h(q')\rangle=[(2\pi)^4/A]\langle|h(q)|^2\rangle\delta^2(q+q')$, we obtain

$$\rho_{e,g}=\left\{\frac{(2\pi)^4}{A}\int_{0<q<Q_c}q^2K_{e,g}(q)^2 \times(1+q^2\zeta_{e,g}^2)^{-2}\langle|z(q)|^2\rangle d^2q\right\}^{1/2} \tag{4}$$

with $\rho\sim\sigma$ since $\langle|z(q)|^2\rangle\sim\sigma^2$. Because $K_{e,g}(q)\leqslant1$, the local slope ρ in the D approximation $[K(q)=1]$ will yield an upper bound for any film thickness ε. Calculations of ρ are shown in Figs. 1 and 2. For large film thickness, we expect

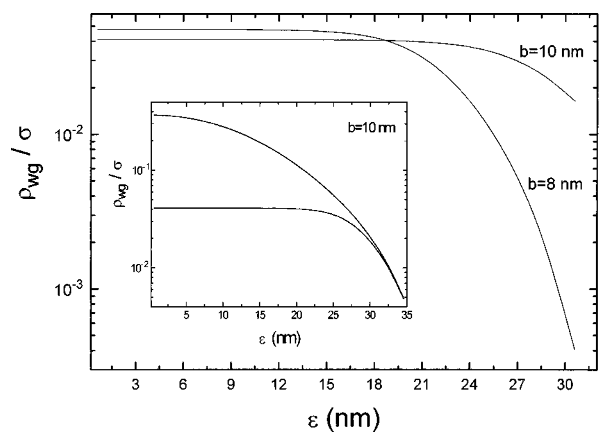

FIG. 1. Schematics of the local interface slope ρ_{wg}/σ vs ε for Gaussian interactions, $a_0=0.3$ nm, $\sigma=1$ nm, $\xi=60$ nm, $\gamma/C_{e,g}=10$ nm^4, and $H=0.4$ for two adjacent values of the potential range b [nonlocal effects; $K(q)\neq1$]. The inset shows ρ_{wg}/σ vs ε of the nonlocal effects [lower curve; $K(q)\neq1$] in comparison with that obtained in the D approximation [upper curve; $K(q)=1$].

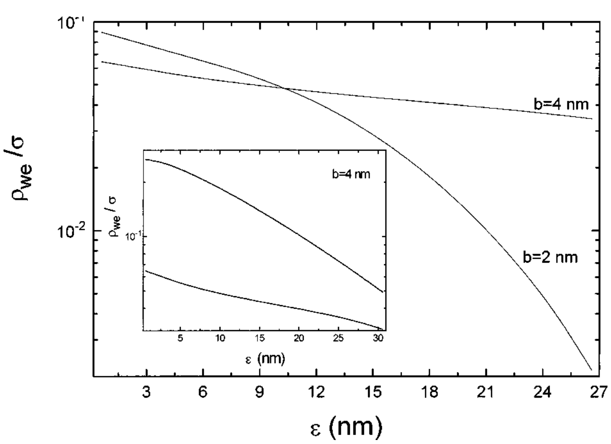

FIG. 2. Schematics of the local interface slope ρ_{we}/σ vs ε for simple-exponential interactions $a_0=0.3$ nm, $\sigma=1$ nm, $\xi=60$ nm, $\gamma/C_{e,g}=10$ nm^4, and $H=0.4$ for two adjacent values of the potential range b [nonlocal effects; $K(q)\neq1$]. The inset shows ρ_{we}/σ vs ε of the nonlocal effects [lower curve; $K(q)\neq1$] in comparison with that obtained in the D approximation [upper curve; $K(q)=1$].

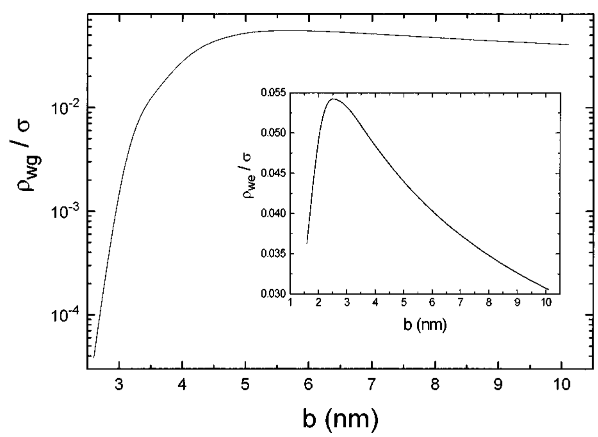

FIG. 3. Schematics of the local interface slope ρ_{we}/σ vs b for Gaussian interactions, $a_0=0.3$ nm, $\sigma=1$ nm, $\xi=60$ nm, $\varepsilon=10$ nm, $\gamma/C_{e,g}=10$ nm^4, and $H=0.4$. The inset shows ρ_{we}/σ vs b for simple-exponential interactions $a_0=0.3$ nm, $\sigma=1$ nm, $\xi=60$ nm, $\varepsilon=10$ nm, and $H=0.4$. In both cases nonlocal effects are considered; $K(q)\neq 1$.

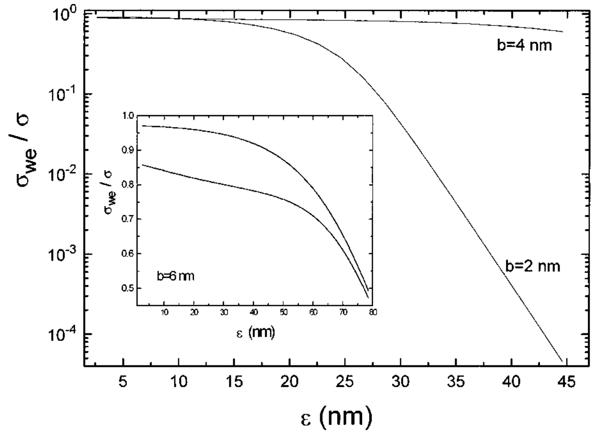

FIG. 5. Schematics of the interface roughness amplitude σ_{we}/σ vs ε for simple-exponential interactions, $a_0=0.3$ nm, $\sigma=1$ nm, $\xi=60$ nm, $\gamma/C_{e,g}=10$ nm^4, and $H=0.4$ for two adjacent values of the potential range b [nonlocal effects; $K(q)\neq 1$]. The inset shows σ_{we}/σ vs ε of the nonlocal effects [lower curve; $K(q)\neq 1$] in comparison with that obtained in the D approximation [upper curve; $K(q)=1$].

intuitively $\rho \ll 1$ since the damping caused by the interface elastic properties occurs at wavelengths much longer than those where substrate roughness shows significant structure $(q>1/\xi)$. The insets of Figs. 1 and 2 depict the comparison with the D approximation (upper curve). For Gaussian interactions, the slope approaches values obtained in the D approximation rather smoothly, while for simple-exponential interactions it remains distinctly lower than that in the D approximation even for the same thickness range and lower potential ranges.

For both exponential interactions, the local slope shows a very sensitive dependence on the interaction range b especially for thick films $(\varepsilon \gg b)$. In the thin film regime $(\varepsilon \approx b)$, the local slope decreases rapidly for low potential ranges. Figure 3 shows the dependence of local slope on the potential range b for a film thickness where significant deviations from the D approximation occur. The observed maximum is significantly steeper for simple-exponential interactions. In both cases, the assumption of weak fluctuations is fulfilled up to very low thicknesses $\varepsilon \approx \sigma$ (assuming σ small). Indeed, numerical solutions of the nonlinear version of Eq. (1) have shown that the liquid interface follows closely the substrate fluctuations even up to thicknesses $\varepsilon \approx \sigma$ where the linear scheme is no longer valid.[1,3]

The linear generalization of the D approximation by inclusion of nonlocal effects leads to a drastic influence on the interface roughness spectrum $\langle |h(q)|^2\rangle_{g,e}$ which is expressed for both exponential and power-law interactions by a rapid exponential decay of long wavelengths $(q\varepsilon \gg 1)$.[1,7] Nevertheless, it remains an open question to what degree the associated to roughness spectrum $\langle |h(q)|^2\rangle_{g,e}$ real space fluctuation properties still keep a strong signature from the nonlocal effects. For this purpose, we will examine the behavior of the rms interface roughness amplitude, and we will compare to that calculated in the D approximation. The rms interface roughness amplitude is given by[13]

$$\sigma_{wg,e}=\left\{\frac{(2\pi)^4}{A}\int_{0<q<Q_c} K_{g,e}(q)^2 \times (1+q^2\zeta_{g,e}^2)^{-2}\langle |z(q)|^2\rangle d^2q\right\}^{1/2}. \qquad (5)$$

Since $K_{e,g}(q)\leq 1$, the amplitude $\sigma_{wg,e}$ will be lower than that in the D approximation $[K(q)=1]$. Figures 4 and 5 depict $\sigma_{wg,e}/\sigma$ vs ε for both types of exponential interactions as well as in comparison with the D approximation (insets; upper curve). Distinct differences appear for these two types of interaction potentials for both the thin and thick film regime. For simple-exponential interactions, the amplitude σ_{we} is more sensitive to changes of the potential effective range b (decaying appreciably faster as b becomes small). Moreover, it can be significantly lower than that in the D approximation even for film thicknesses larger than the substrate roughness correlation length $(\varepsilon>\xi)$. By contrast, for Gaussian interactions the amplitude σ_{wg} approaches

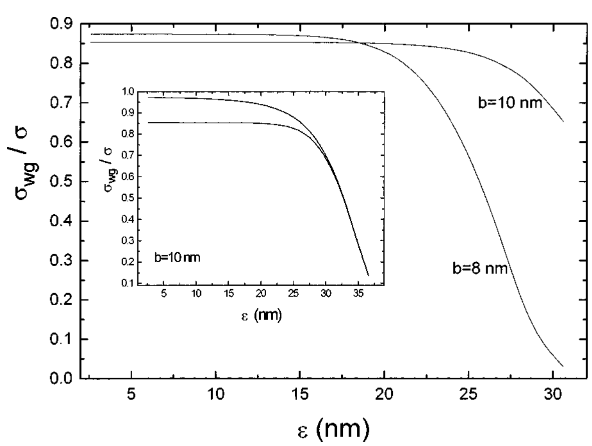

FIG. 4. Schematics of the interface roughness amplitude σ_{wg}/σ vs ε for Gaussian interactions, $a_0=0.3$ nm, $\sigma=1$ nm, $\xi=60$ nm, $\gamma/C_{e,g}=10$ nm^4, and $H=0.4$ for two adjacent values of the potential range b [nonlocal effects; $K(q)\neq 1$]. The inset shows σ_{wg}/σ vs ε of the nonlocal effects [lower curve; $K(q)\neq 1$] in comparison with that obtained in the D approximation [upper curve; $K(q)=1$].

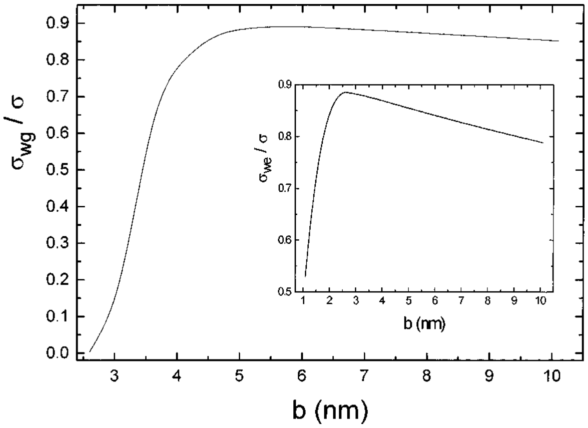

FIG. 6. Schematics of local interface roughness amplitude σ_{wg}/σ vs b for Gaussian interactions $a_0=0.3$ nm, $\sigma=1$ nm, $\xi=60$ nm, $\varepsilon=10$ nm, $\gamma/C_{e,g}=10$ nm^4, and $H=0.4$. The inset shows σ_{we}/σ vs b for simple-exponential interactions $a_0=0.3$ nm, $\sigma=1$ nm, $\xi=60$ nm, $\varepsilon=10$ nm, and $H=0.4$. In both cases nonlocal effects are considered; $K(q)\neq 1$.

faster the behavior predicted within the D approximation for rather moderate film thicknesses ($b<\varepsilon<\xi/2$).

The dependence of the amplitudes $\sigma_{wg,e}$ on the potential range b is depicted in Fig. 6. A maximum is observed with steeper behavior for simple-exponential interactions (similarly with the local interface slope). In the latter case, the roughness amplitude decreases significantly faster as the potential interaction range increases and approaches values close to the film thickness ($b\sim\varepsilon$). Therefore, slower decaying interactions will induce more drastic nonlocal effects on the interface fluctuations. Finally, remarks similar to those for $\sigma_{wg,e}$ will hold also for the height-height correlation function $C_{wg,e}(r)\propto\int\langle|h(q)|^2\rangle_{g,e}e^{-i\mathbf{q}\cdot\mathbf{r}}d^2q$ which is expected since the maximum of $C_{wg,e}(r)$ is $\sigma^2_{wg,e}$ that clearly depicts the significance of the short wavelength damping due to nonlocal effects.

In conclusion, we investigated nonlocal effects on real space fluctuation properties of liquid films, which completely wet self-affine rough substrates, for exponential interactions $U(r)\sim e^{-ar^n}$ ($n=1,2$). Although a similar behavior is expected qualitatively with interactions without any intrinsic length scale, for exponential interactions the crossover to the surface tension dominated regime occurs at smaller film thicknesses. Moreover, it was shown that the intrinsic length scale of the interaction potential and the potential form can have strong impact on the real space fluctuation properties for relatively thin liquid layers. In fact, the interface roughness amplitude and local slope show a maximum as a function of the effective potential range which is steeper for simple-exponential interactions. In the latter case, more pronounced differences appear in comparison with the D approximation where nonlocal effects are ignored.

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